Low Temperature Atomic Layer Deposition of Tin Dioxide, SnO\(_2\)

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Outline

Earth-abundant, non-toxic transparent conductor: SnO_2

ALD process for SnO_2

- **new tin precursor**
- **growth per cycle**

SnO_2 film properties

- **composition**
- **structure**
- **optical properties**
- **electrical properties**
- **applications**

SnO_2: Transparent Conductor and Heat Mirror

High visible transmission (high bandgap (E_g ~ 4.1 eV)

High electrical conductivity (high electron concentration and mobility)

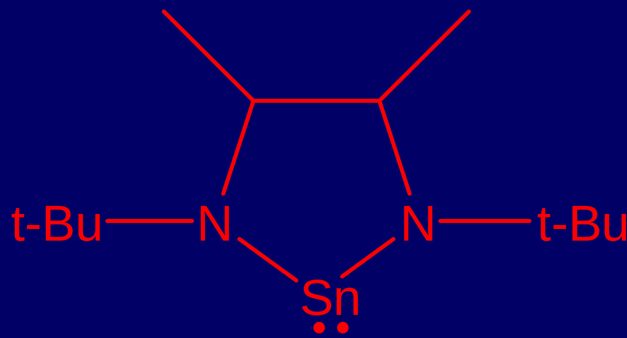
High environmental stability

Constituent elements are non-toxic and abundant

Known ALD processes require high temperatures, > 200 ^{o}C

or produce impure films (C, N), amorphous, low conductivity

Tin(II) Cyclic Stannylene as ALD Precursor



N^2,N^3-di-*tert*-butyl-butane-2,3-diamido-tin(II)

Hydrocarbon ligand => high volatility (30 Torr at 60 ºC)

Chelate structure => thermal stability

Sn-N bonds => reactive to hydrogen peroxide, H_2O_2

Synthesis and properties described by Adam Hock, Wednesday 14:15

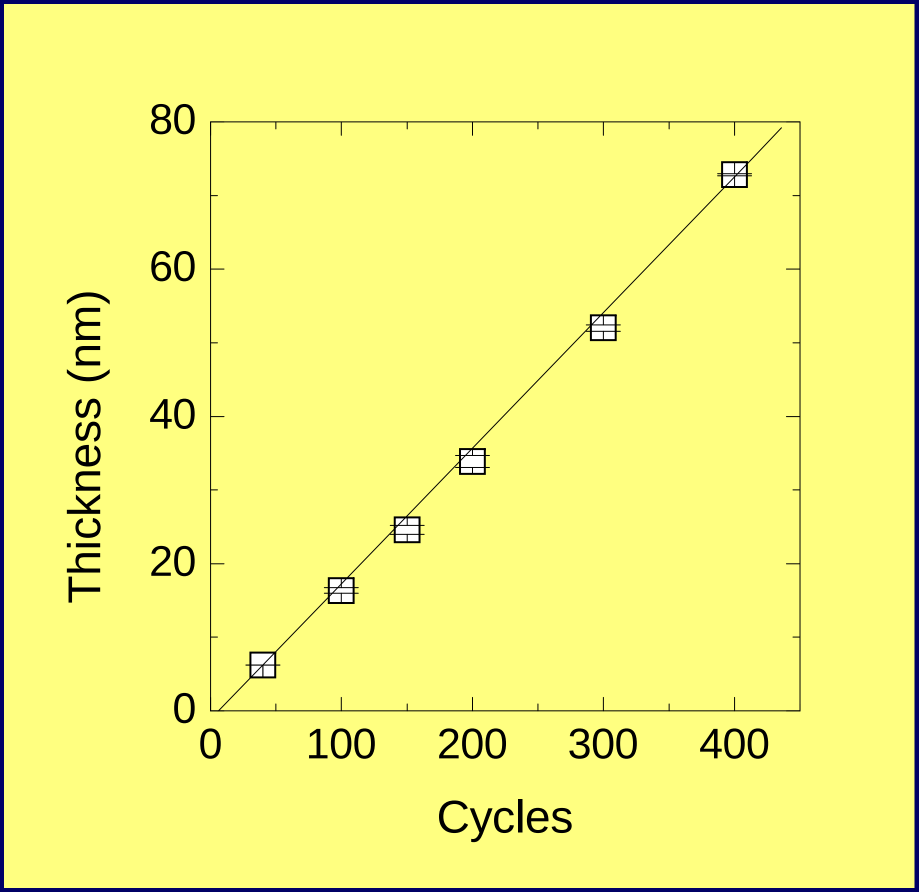
ALD Process for SnO_2

Source temperature: 40 °C

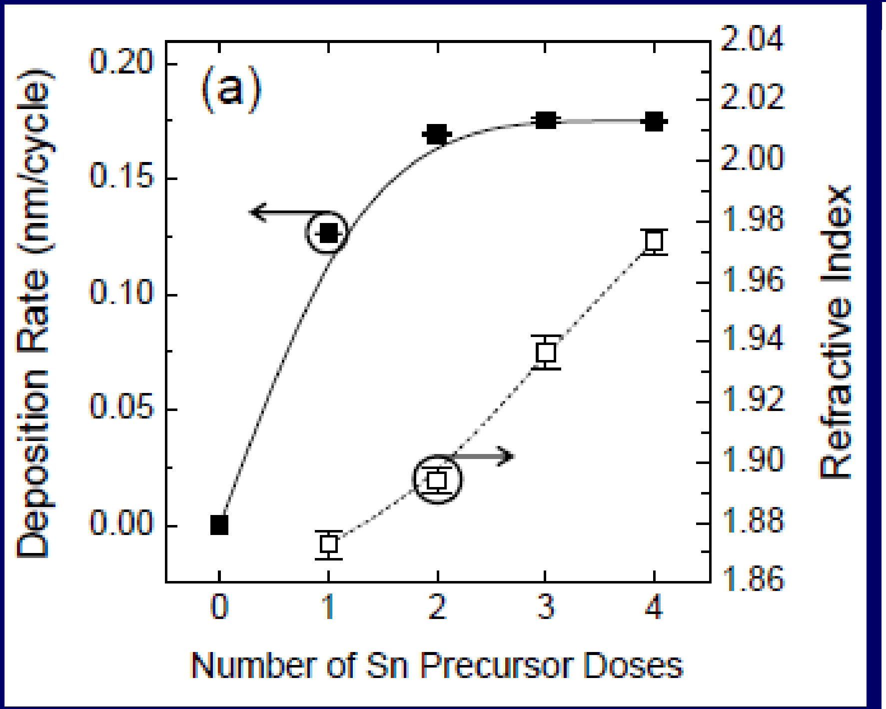
Substrate temperature: 120 °C

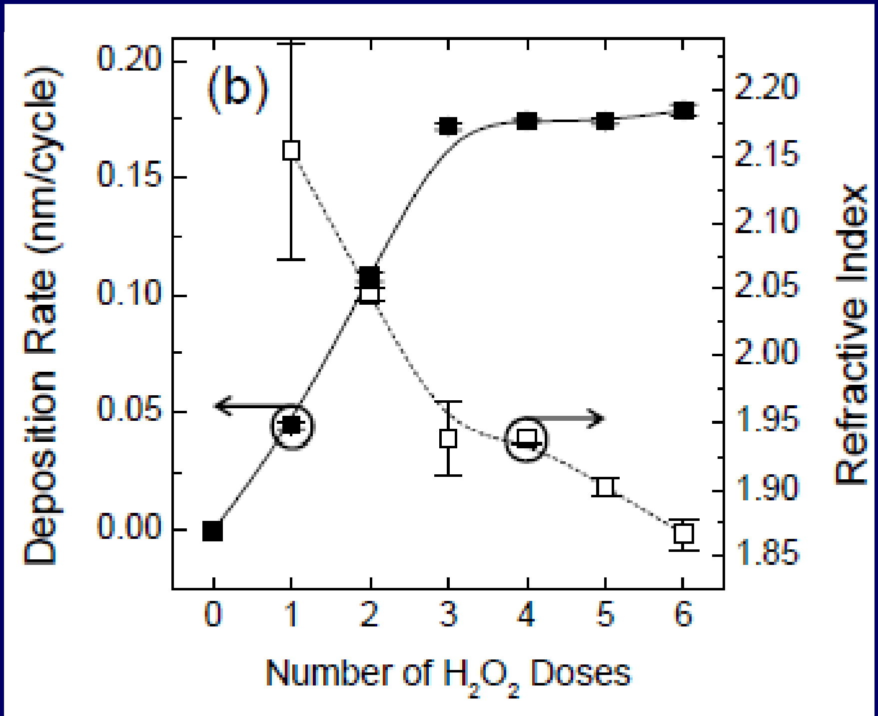
Growth per cycle: 0.18 nm

Induction period: only a few cycles



ALD Saturation Curves



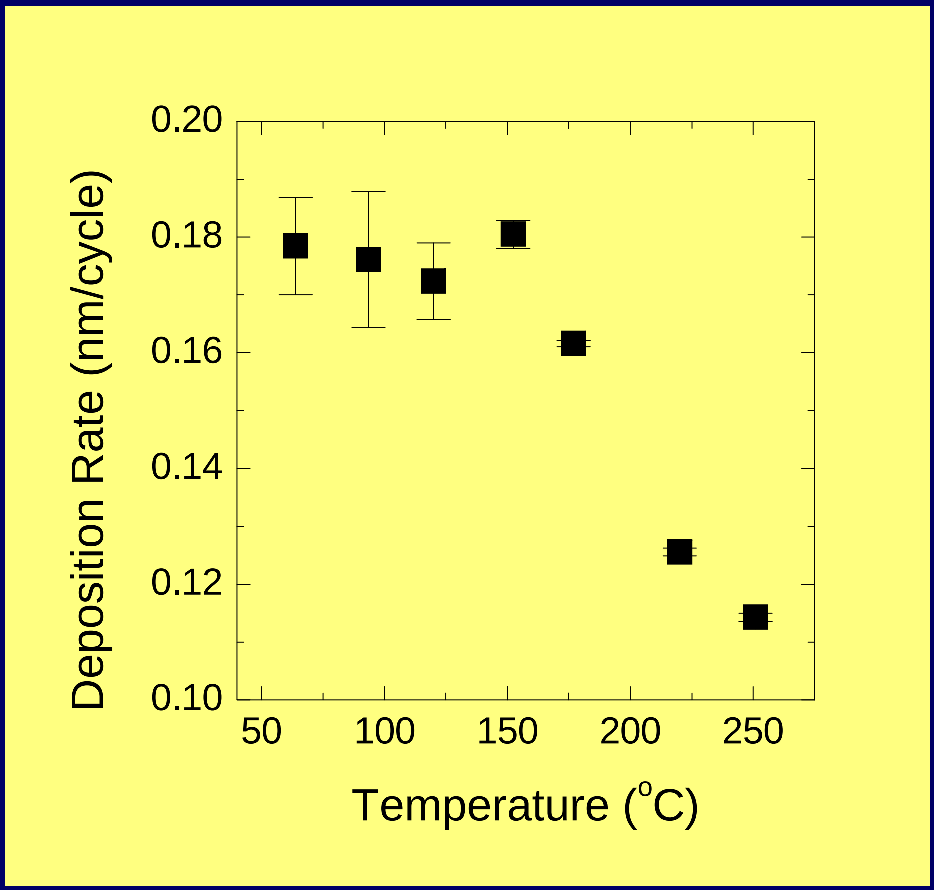


Increasing doses of cyclic stannylene precursor for tin

Increasing doses of oxygen precursor, hydrogen peroxide

Refractive index ~ 1.94 for saturated growth (3 doses)

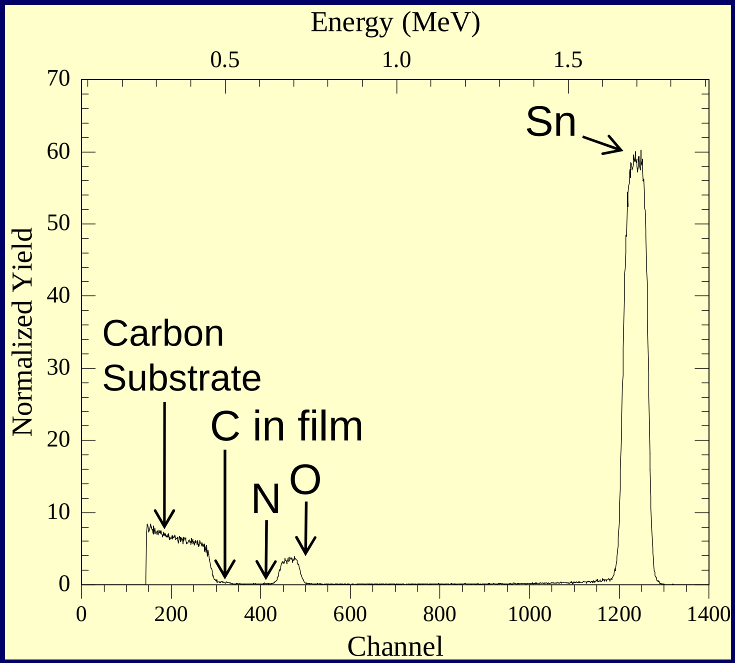
Temperature Dependence of Growth

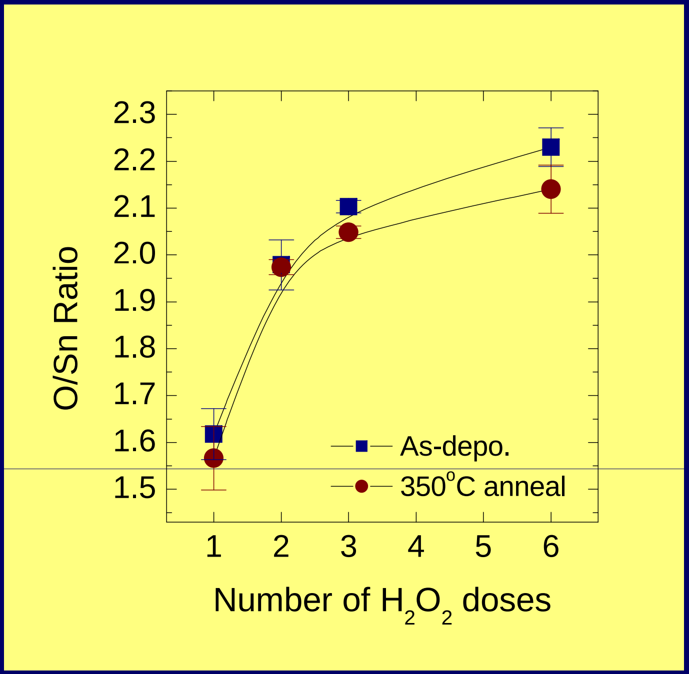


ALD window from 50 to 150 °C

SnO_x Composition

Rutherford Backscattering Spectroscopy (RBS)



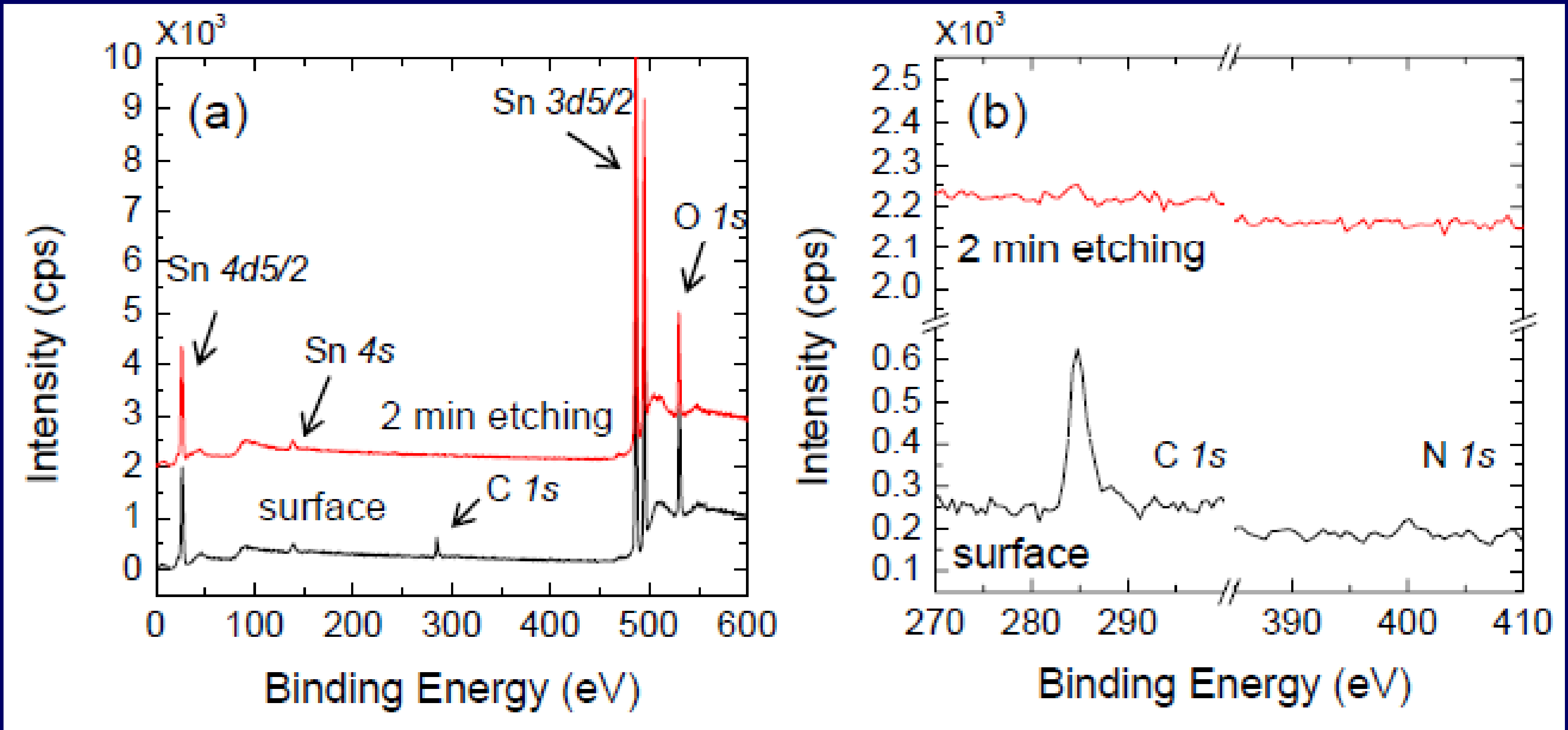


No C or N in film

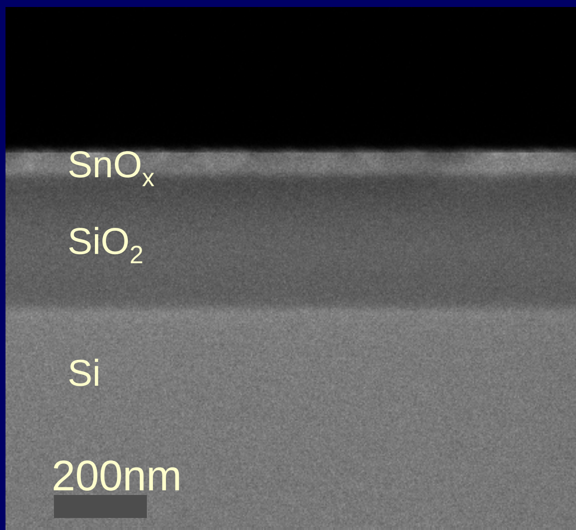
SnO_2 for 2-3 doses

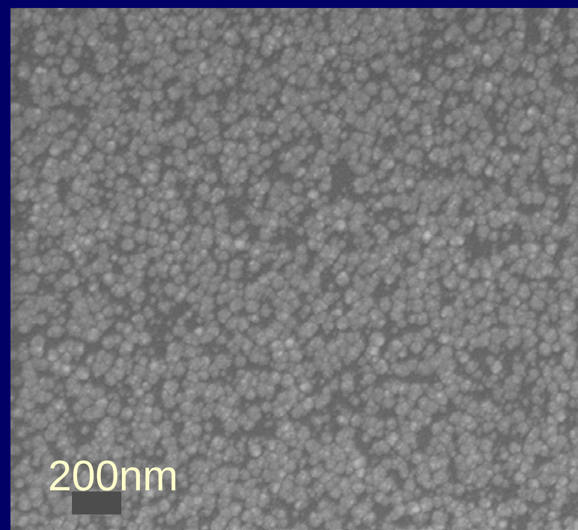
X-Ray Photo-Electron Spectroscopy (XPS)

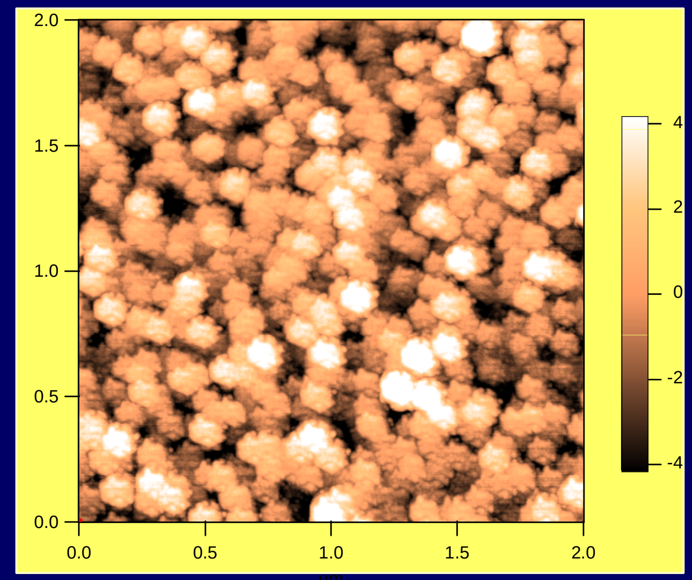
No impurities detected (C, N) inside film



Smooth Morphology of SnO_2 Films





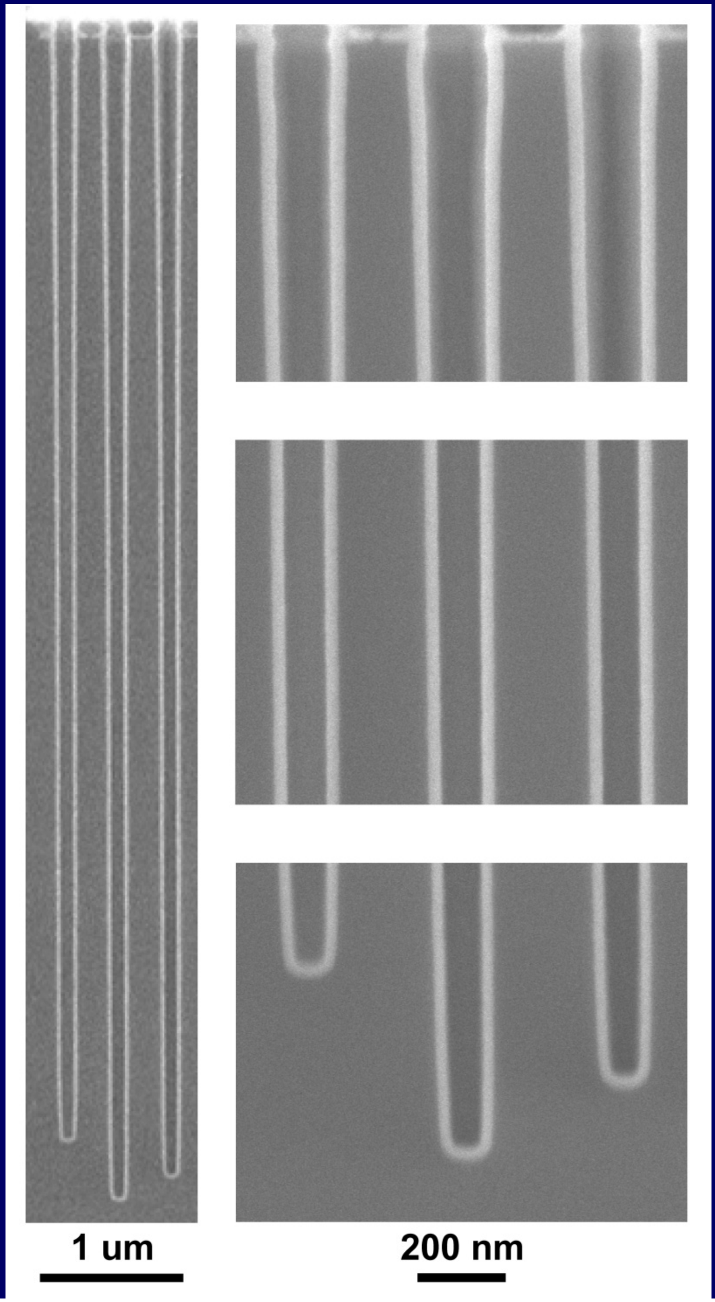


400 cycles => 71 nm

AFM
RMS roughness = 2 nm
< 3 % of thickness

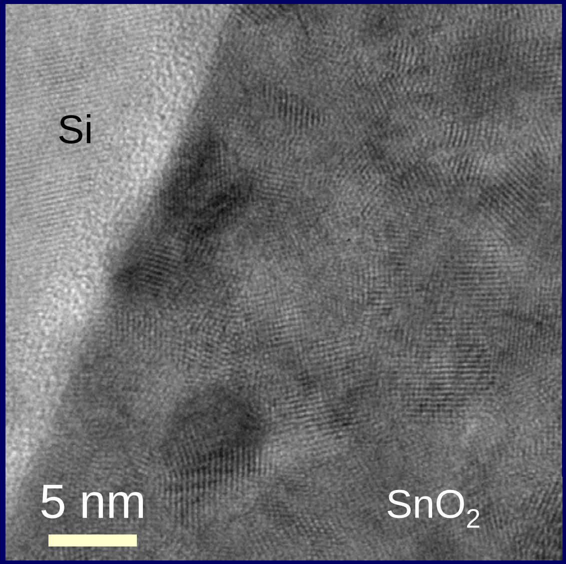
Step Coverage

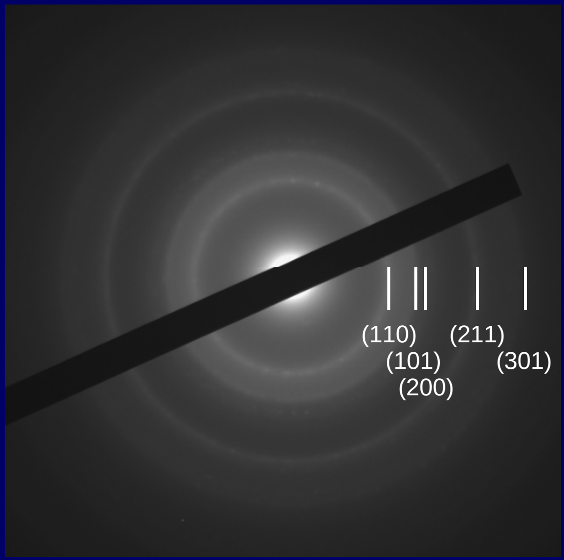
Uniform thickness in holes with aspect ratio 50:1, grown at 50 ^oC



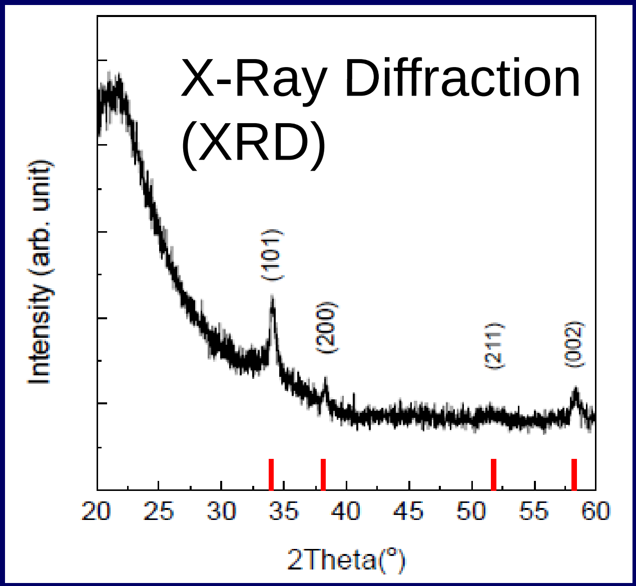
Polycrystalline Rutile Structure of SnO_2 Films

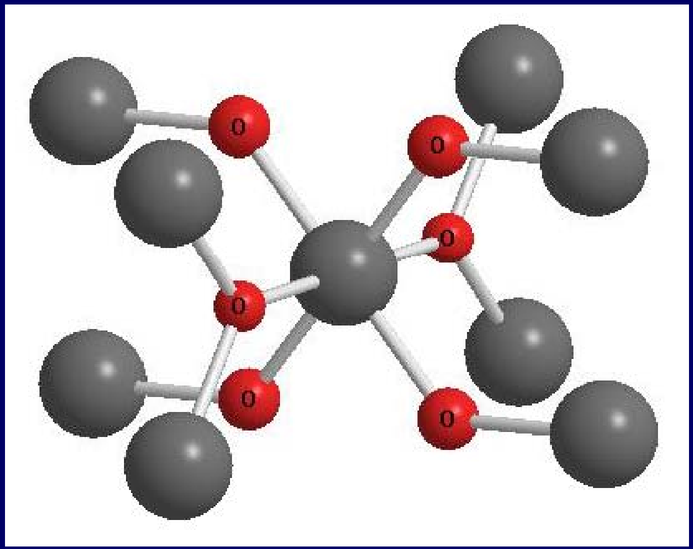
TEM



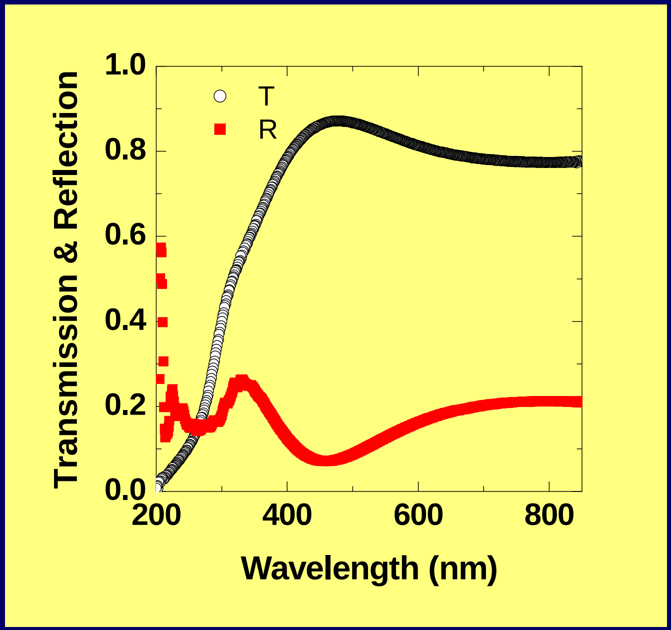


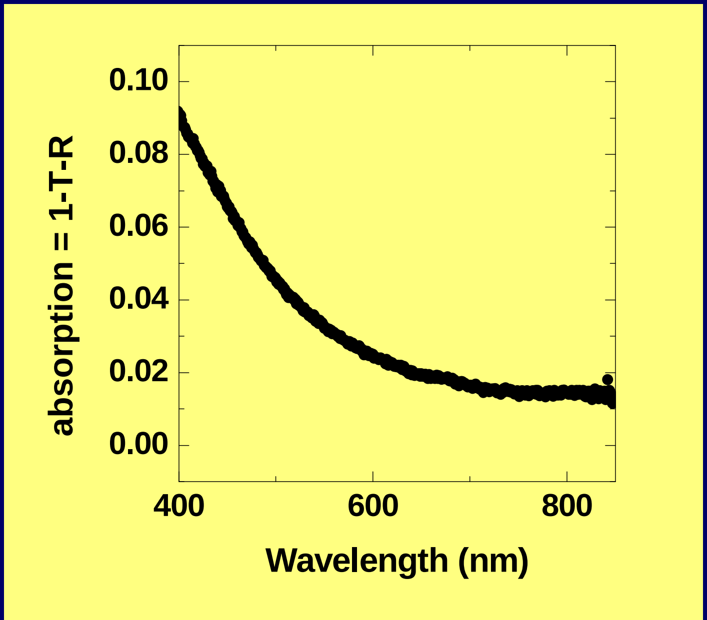
electron diffraction





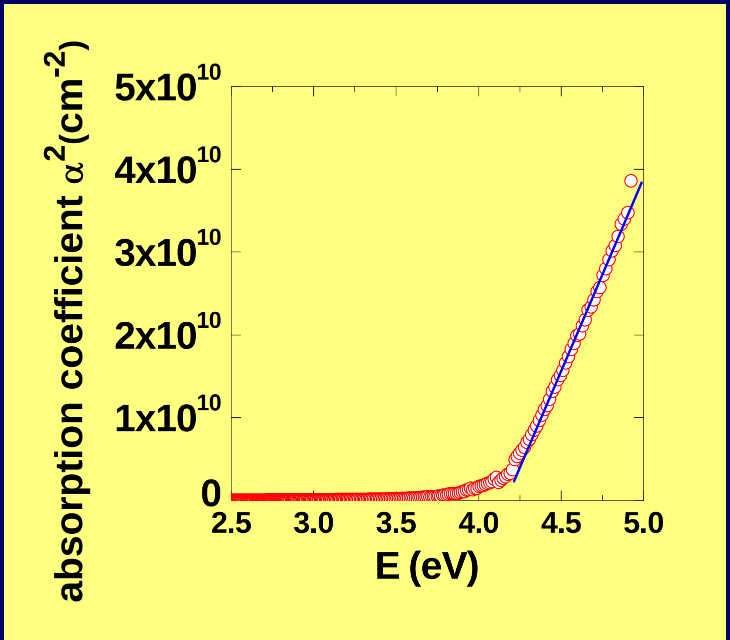
SnO_2 has Very Little Visible Absorption





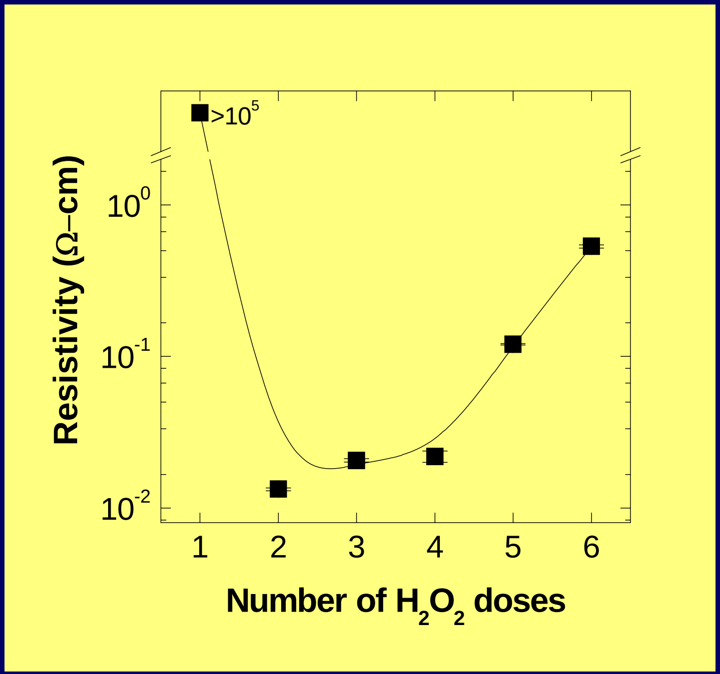
film 100 nm thick

Band gap 4.13 eV



Electrical Properties

Resistivity minimum for stoichiometric SnO_2 (2 to 4 doses)

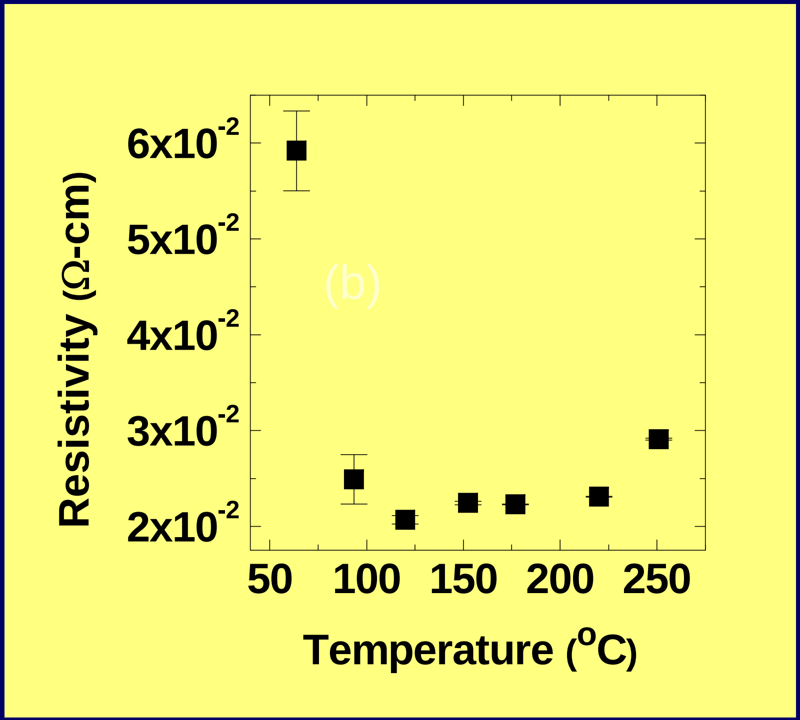


N-type semiconductor by Hall measurements

electron concentration ~ 10^{20} cm^{-3}

electron mobility ~ 6 cm^{2} V^{-1} s^{-1}

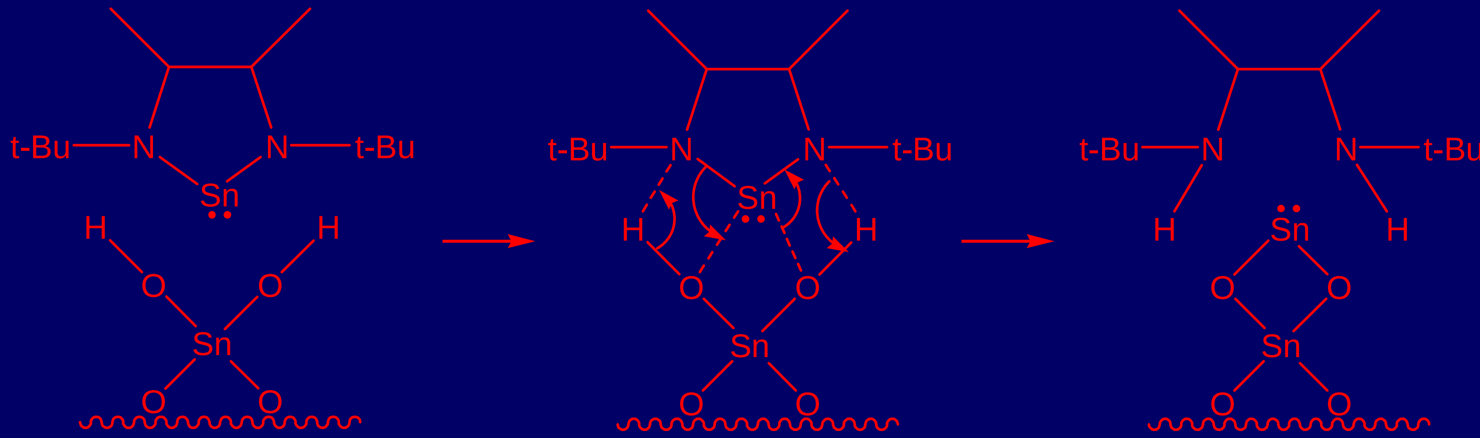
Resistivity vs. Deposition Temperature



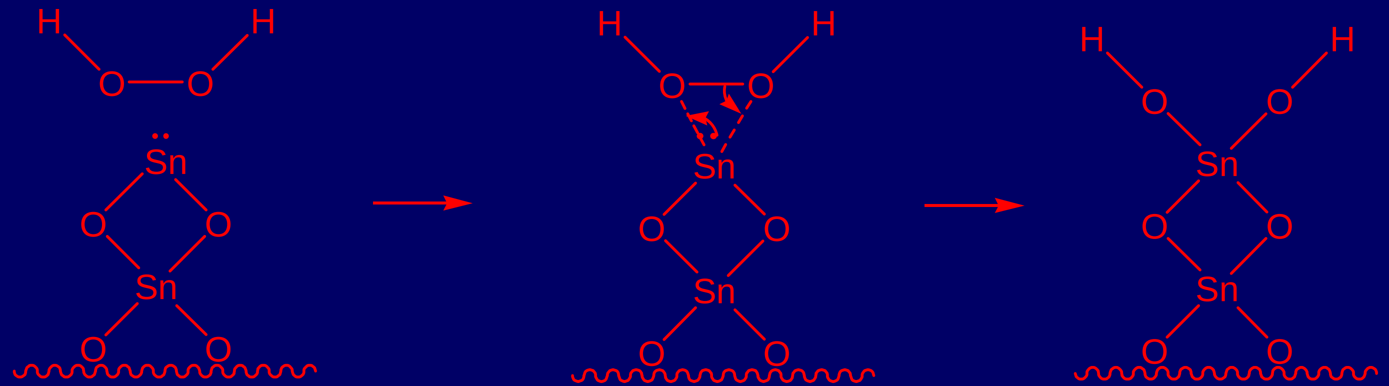
minimum resistivity 0.02 Ω-cm when deposited at 120 °C

Proposed Mechanism

Ligand exchange of Sn precursor with hydroxylated surface



Oxidative addition of hydrogen peroxide



Summary

SnO_2 is transparent semiconductor made of earth-abundant, inexpensive, non-toxic elements

ALD from a cyclic tin(II) amide and H_2O_2 => SnO_2

Smooth films of pure, stoichiometric, polycrystalline SnO_2

High optical transparency and electrical conductivity

Successfully used in several applications:
- organic solar cells (with Alan Heeger, UCSB)
- conducting and protective coatings for plastics (with Michelle Schulberg, Physical Sciences Inc.)
- electron multipliers (Philippe deRouffignac, Arradiance, to be presented on Wednesday at 13:30)

another possible application: thin-film transistors on plastic

Acknowledgements

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